

**TITLE:** INVESTIGATION OF NO<sub>x</sub> REMOVAL FROM SMALL  
ENGINE EXHAUST

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**FINAL REPORT**

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# INVESTIGATION OF NO<sub>x</sub> REMOVAL FROM SMALL ENGINE EXHAUST

## ABSTRACT

Contribution of emissions from small engines to the air pollution is significant. Due to differences in operating conditions and economics, the pollution control systems designed for automobiles will be neither suitable nor economically feasible for use on small engines. The objective of this project was to find a catalyst for the removal of NO<sub>x</sub> from the exhaust of small engines which use a rich air to fuel ratio. The desired catalyst should be inexpensive so that the cost of the pollution control unit will be only a small fraction of the total equipment cost.

The high cost of noble metals makes them too expensive for use as NO<sub>x</sub> catalyst for small engines. Catalytic reduction of NO can also be accomplished by base-metal oxide catalysts. The main disadvantage of base-metal catalysts is their deactivation by poisons and high temperatures. Requirements for the length of the life of the small engine exhaust catalysts are much less than those for automobile exhaust catalysts. Since there is no oxygen in the exhaust gases, reduction selectivity is not a problem. Also, the reducing exhaust gases might help prevent the harmful interactions of the catalyst with the support. For these reasons only the supported metal oxide catalysts were investigated in this project.

In the first stage of this research, several samples of supported CuO, NiO, CuCr<sub>2</sub>O<sub>4</sub>, and NiCr<sub>2</sub>O<sub>4</sub> catalysts were prepared by impregnation of the support.  $\gamma$ -alumina pellets and small hollow  $\gamma$ -alumina cylinders (sections of small diameter alumina tubing) were used as catalyst supports. The performances of these catalysts were investigated in a laboratory scale fixed bed reactor, using simulated exhaust gases containing methane as the hydrocarbon. An experimental setup was designed and constructed for this purpose.

In dry gas, complete conversion of NO was obtained above 220°C with the supported copper oxide catalyst. Copper chromate catalyst produced complete conversion above 600°C, while complete conversion was obtained above 450°C with the nickel oxide catalyst. Copper oxide catalyst is by far the most active catalyst for the dry reduction of NO. The effect of temperature on conversion

suggests that the activation energy for NO reduction on CuO catalyst is much higher than those on copper chromate and nickel oxide.

Presence of 7% water vapor in the gas resulted in significant deactivation of the catalysts. With the copper catalyst NO conversion in wet gas was only about 65% at 700°C. A very similar behavior was observed with the copper chromate catalyst. The reduction of NO in wet gas appears to have the same rate and activation energy on copper oxide and copper chromate catalysts. Nickel oxide catalyst appears to be almost completely deactivated by wet gas. It was observed that some activity was restored when the water was switched off, but most of the deactivation appears to be permanent. This work was presented at the AIChE Annual Meeting in Chicago, IL, November 1996.

In the second stage, two new types of catalysts, supported cerium oxide and supported cerium oxide/copper oxide, were prepared and tested using the same simulated exhaust gas. The selection of the new catalysts was based on our experience with the supported ceria catalysts and on recent selective catalytic reduction studies with cerium-containing catalysts. The performances of the prepared catalyst samples were investigated in the laboratory fixed-bed reactor. Cerium oxide catalyst was found to be significantly inferior to copper oxide catalysts both with dry and wet gases. On the other hand, mixed oxide catalysts containing copper and cerium oxides proved to be better catalysts with wet gases probably due to the inhibition of the reduction of copper oxide. These results were presented at the AIChE Annual Meeting in Los Angeles, CA, November 1997.

In the final stage, some selected catalysts were tested using two different exhaust gas compositions; One containing propylene instead of methane as the hydrocarbon, and the other containing carbon monoxide and hexane and simulating the actual exhaust gas composition supplied by Briggs and Stratton. Nitric oxide reduction with propylene was obtained at lower temperatures with all catalysts. Increasing the copper fraction in the catalyst and increasing the propylene to nitric oxide ratio lowered the reduction temperature. On the other hand catalysts containing higher fractions of cerium tended to be more resistant to sulfur poisoning. The performance of the catalysts with the simulated Briggs and Stratton exhaust gas mixture were significantly superior. Complete NO reduction was obtained with gases not containing SO<sub>2</sub> even at 473 K. Exhaust gases containing SO<sub>2</sub> required higher

temperatures for complete reduction of NO.

## OBJECTIVES

The objective of this research was to find a catalyst for the removal of NO<sub>x</sub> from the exhaust of small engines which use a rich air to fuel ratio. The desired catalyst should

- be able to decrease the NO<sub>x</sub> content of the exhaust gases to less than four grams per brake horsepower-hour which is the 1999 standard set by the California Air Resources Board<sup>(1)</sup>,
- be inexpensive so that the cost of the entire pollution control unit is a small fraction of the total equipment cost,
- contribute to, (or at least not interfere with) the removal of CO and hydrocarbons,
- be resistant to catalyst poisons such as sulfur and phosphorus contained in the fuel or engine oil,
- have sufficient structural strength to resist attrition, and
- not be toxic.

The catalyst bed should produce only a small pressure drop and should contribute to acoustic damping of the exhaust noise.

## INTRODUCTION

Contribution of emissions from small engines such as those in lawn equipment to air pollution is significant. Due to differences in operating conditions and economics, the pollution control systems designed for automobiles will be neither suitable nor economically feasible for use on small engines. If the pollution from these engines is to be controlled, new cost effective, specially designed systems are required. Automobile engines operate with a slightly lean air to fuel ratio or the engines' air-fuel mixture is strictly controlled within a small air/fuel ratio window around the stoichiometric value. The small engines under consideration, however, operate with a slightly rich air/fuel ratio. This, of course, produces an exhaust gas composition devoid of oxygen and containing significant amounts of

carbon monoxide together with some unreacted hydrocarbons. If elimination of the carbon monoxide and unreacted hydrocarbons are also desired, a specially designed catalyst bed will be needed to introduce air at some intermediate point. In addition, small engine catalytic converters must cost a lot less than those for automobiles for them to be economically feasible. This requirement alone precludes the use of noble-metal catalysts for small engines. Also, the reducing exhaust gases might prevent the harmful interaction of the base-metal catalysts with the alumina support.

## **BACKGROUND INFORMATION**

In the first phase of this project, some common base metal oxides supported on alumina were tested as NO reduction catalysts. A helium-methane mixture was used as the reductant. The methane concentration was determined by increasing the methane mole ratio until no further significant increase was noted in the conversion of NO. The following conclusions were reached: In dry gas, complete conversion of NO was obtained above 493 K with the supported copper oxide catalyst. Copper chromate catalyst produced complete conversion above 873 K, while complete conversion was obtained above 723 K with the nickel oxide catalyst. Copper oxide catalyst was by far the most active catalyst for the dry reduction of NO. The effect of temperature on conversion suggests that the activation energy for NO reduction on CuO catalyst is much higher than those on copper chromate and nickel oxide.

Presence of 7% water vapor in the gas resulted in significant deactivation of these catalysts. With the copper catalyst NO conversion in wet gas was only about 65% at 700°C. A very similar behavior was observed with the copper chromate catalyst. The reduction of NO in wet gas appeared to have the same rate and activation energy on copper oxide and copper chromate catalysts. Nickel oxide catalyst was almost completely deactivated by wet gas. It was observed that some activity was restored when the water was switched off, but most of the deactivation appeared to be permanent. Visual observation of the spent catalyst indicated a change in the color to reddish black, which led to the conclusion that the reduction of the oxide to metal may be the cause of the deactivation of the catalyst.

Since ceria improves the resistance of the alumina support to thermal sintering, it has been a component of the automobile catalysts for some time. There are a few patents<sup>1,2,3</sup> which indicate that ceria possesses sufficient activity and selectivity as a catalyst for the reduction of NO with NH<sub>3</sub> in the presence of oxygen at relatively high temperatures (above 723 K). An investigation<sup>4</sup> of unsupported ceria and copper oxide-ceria sorbent/catalysts report that with Cu-Ce sorbents, 90% NO<sub>x</sub> removal efficiencies could be obtained at 400°C in the presence of O<sub>2</sub> and SO<sub>2</sub>.

A recent development in this area is the use of metal-exchanged zeolites as catalysts for this purpose. In particular Cu/ZSM-5 and Co/ZSM-5 have shown significant activity for NO<sub>x</sub> reduction by hydrocarbons in the presence of oxygen. Although Cu/ZSM-5 is very effective with higher hydrocarbons, it has no selectivity for the SCR reaction with methane. One disadvantage of the zeolite-based catalysts is that they have a limited range for nitric oxide reduction around 700-800 K. Another is the severe deactivation by the water present in the flue gas. Recently Zhang et al.<sup>5</sup> reported that the incorporation of cerium ions into Cu/ZSM-5 stabilized the active copper sites for NO decomposition in wet gases by suppressing CuO formation and improved the hydrothermal stability of the catalyst. The high selectivity of cerium for the selective catalytic reduction of nitric oxide with methane, combined with the high activity of copper for nitric oxide reduction resulted in improved catalyst performance.

Some metal oxides were, also, shown to possess sufficient activity and selectivity for NO reduction with methane in the presence of oxygen. The activity of Li/MgO catalyst for NO reduction with methane was equal to that of Co/ZSM-5 but required higher temperatures and did not exhibit a NO conversion bend-over with temperature<sup>6</sup>. The selectivity for N<sub>2</sub> production was 60% at 893 K and increased with temperature.

In another study<sup>7</sup>, La<sub>2</sub>O<sub>3</sub> was found to be more active and selective for nitric oxide reduction by methane than the magnesium oxide-based catalysts, with essentially 100% selectivity toward nitrogen production. Its activity increased continuously with temperature with no bend-over up to 973 K. The specific activity (based on the catalyst area) of La<sub>2</sub>O<sub>3</sub> at 773 K was comparable to that of Co/ZSM-5. Ceria is a fluorite-type oxide like La<sub>2</sub>O<sub>3</sub>, with superior oxygen vacancy and mobility

properties. In low temperature fuel gas desulfurization applications, addition of cerium oxide to copper oxide sorbents is known to inhibit the reduction of copper oxide to metal.

These observations indicated a possibility of developing a ceria-based sorbent/catalysts for the removal of nitrogen oxides from small engine exhaust. The ceria-based catalyst was expected to have a potential for the reduction of nitrogen oxides to nitrogen with methane and to reduce the deactivation of copper oxides by wet gases and sulfur. Under reducing conditions copper oxide is reduced and copper is easily sulfided by  $\text{H}_2\text{S}$ . Therefore, it may be prone to sulfur poisoning. On the other hand ceria is not reduced to atomic cerium under the conditions of the experiment and cerium sulfide is not formed. In addition, the presence of ceria was expected to inhibit the reduction of copper oxide to metallic copper, thus reducing sulfide formation. Therefore, ceria was expected to be resistant to sulfur. Cerium is slightly more expensive than copper, but it is expected that due to the anticipated high space velocities (about 90000/hr), the amount of catalyst to be used will not be large enough to make this price differential prohibitive.

## WORK DONE

In this phase of the investigation, several samples of supported  $\text{CuO-CeO}_2$  catalysts were prepared by impregnation of the support with an aqueous solution of the appropriate metal salts and the subsequent calcination without air flow. Spherical  $\gamma$ -alumina pellets were used as catalyst supports. The performances of these catalysts were investigated in a laboratory scale fixed bed reactor, using various simulated exhaust gases. The initial experimental setup consisted of a feed preparation section containing manual metering valves for the adjustment of gas flow rates, electronic mass flow meters, and solenoid valves for flow switching; a laboratory scale quartz fixed bed reactor; and a gas sampling system to provide samples for the gas chromatograph and the chemiluminescence  $\text{NO}_x$  analyzer. This setup was used for the catalyst screening tests using methane as the reductant. The tests using propylene as the reductant and the tests using the simulated Briggs and Stratton exhaust gas were performed on the new setup with electronic flow controllers, improved water vapor feeder, and direct sampling for the gas chromatograph.



The reactor was placed in a temperature-controlled tubular furnace. The gas temperature at the bed entrance was measured by a thermocouple. A differential pressure gauge indicated the pressure difference across the reactor. For the flow rates and catalyst amounts used, this pressure change was observed to be very small even though small catalyst particles were used. Therefore, for similar space velocities, since larger catalyst pellets would be used in practice, pressure loss across the catalyst bed is not expected to be a problem.

The NO and NO<sub>x</sub> in the reactor exhaust were measured by a Thermoenvironmental Model 42H Chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer and the CO, CO<sub>2</sub> and N<sub>2</sub> by a Varian 3400 Gas Chromatograph equipped with the Star data acquisition and analysis system. The NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer contains a high temperature (923 K) NO<sub>2</sub> to NO converter. It was found that in the absence of oxygen, in this converter significant reaction of NO<sub>x</sub> with the reductant took place, thus rendering the NO<sub>2</sub> measurements unreliable. For the tests with the new experimental setup, a low temperature (623 K) NO<sub>2</sub> to NO converter was also purchased. Measurements using the low temperature converter were reliable and did not indicate any significant NO<sub>2</sub> formation.

The standard experimental conditions used in the experiments with methane as reductant were:

Gas composition:	NO : 850 ppm
	CH <sub>4</sub> : 4000 ppm
	H <sub>2</sub> O : 6.5 - 7%
	He : Balance
Gas temperature:	673 – 973 K
Space velocity:	40,000 h <sup>-1</sup> (Gas flow rate: 700 cc/min)
Catalyst:	CeO <sub>2</sub> -CuO catalysts
Catalyst support:	Spherical γ-alumina particles, 1/16 inch in diameter
Metal loading on catalyst:	10%
Catalyst mass:	2 g.

The standard conditions used in the experiments with propylene as reductant were:

Gas composition:	NO : 800 ppm
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	Propylene:	800 ppm
	H <sub>2</sub> O :	7%
	He :	Balance
Gas temperature:	573 – 973 K	
Gas flow rate:	750 cc/min	
Catalyst:	CeO <sub>2</sub> -CuO catalysts	
Catalyst support:	Spherical $\gamma$ -alumina particles, 1/16 inch in diameter	
Metal loading on catalyst:	10%	
Catalyst mass:	2 g.	

The composition of the simulated Briggs and Stratton exhaust gas was:

CO:	4 %
Hexane	350 ppm
NO:	500 ppm
H <sub>2</sub> O:	12 %
Balance:	Helium

Other conditions were the same as those of the runs with propylene.

## RESULTS

The catalysts prepared and their properties are summarized in Table 1. In all the catalysts tabulated in Table 1, ALCOA CSS200 1/16"  $\gamma$ -alumina particles were employed as support. The 10 % metal loading corresponds roughly to monolayer coverage of the support, which has a surface area of 200 m<sup>2</sup>/g.

**TABLE 1. Catalyst Properties**

<b>CATALYST</b>	<b>Metal Loading, mass %</b>		<b>Surface Area, m<sup>2</sup>/g</b>
	<b>Ce</b>	<b>Cu</b>	
CAT-CU5-II	0	4.57	113
CAT-CU5-IV	0	4.57	
CAT-CU5CE5-II	4.58	5.54	122
CAT-CU3CE1-I	2.26	8.42	134
CAT-CU4CE1-I	1.90	8.76	130
CAT-CU1CE3-I	6.49	2.77	122

Results from the NO reduction experiments in the presence of water and methane as the reductant are presented in figures 1-3. These figures indicate that as copper to cerium ratio increases, conversion of NO is enhanced and complete conversion is approached. As was expected, conversion increases with a reduction in space velocity. Additional experiments also indicated that ceria by itself is not a good catalyst for the reduction of NO in the absence of oxygen both in dry and wet gases. On the other hand, addition of cerium oxide to copper oxide catalysts exhibited enhanced catalytic activity with wet gases. Used catalysts had about the same color as the fresh catalysts. Catalysts with copper to cerium ratio of less than 3 are inferior to copper. Catalysts with copper to cerium ratio higher than 3 have higher activities than copper oxide especially at lower temperatures. Catalyst with a copper to cerium ratio of 4 exhibits the best wet performance, corresponding to 95% NO conversion at 600°C.

Figure 4 presents the effect of the reductant (methane) concentration on NO reduction. There appears to be an optimum reductant concentration, which corresponds to a maximum in NO conversion, but the effect of methane concentration beyond the optimum is not very significant.

Mr. Ralph Stevens from the Electronics Fabrication Division at NASA Langley Research Center took photographs of the catalyst samples cited in Table 1 using a Scanning Electron Microscope with the EDAX (Energy Dispersive X-Ray) facility. Representative micrographs are presented in Figure 5, which revealed that the crystallite size for the CU6CE1 catalyst is larger than that for Cu3Ce1 catalyst. EDAX results show how the active metal is distributed on the support and presented for CAT-CU6CE1 in Figure 6.

It may be observed that copper is more uniformly distributed in the catalyst particle than cerium, which has mainly concentrated on the outer edges of the support particle in an egg-shell distribution pattern. The more uniform distribution of copper is due to the presence of cerium. It was observed during the preparation procedure that the aqueous solution of the cerium salt is oily and more viscous than that of the copper salt. Higher viscosity may be the governing factor in dispersing the copper salt and slower diffusion of the cerium salt. Table 2 presents the metal distribution in the other catalysts.

This work was presented at the AIChE Annual Meeting in Los Angeles, CA, November 1997.

TABLE 2. Distribution of Components in the Catalysts (See Figure 6 for locations)

Component	Mass% at 0 (avg)	Mass% at 1	Mass% at 2	Mass% at 3
<b>CAT-CU3CE1</b>				
O	29.80	21.50	21.76	
Al	41.00	54.00	52.41	
Ce	11.27	7.62	10.72	
Cu	17.86	16.88	15.12	
Cu/Ce	1.58	2.21	1.41	

CAT-CU4CE1				
O	22.35	14.67		
Al	50.82	52.13		
Ce	10.04	11.30		
Cu	16.79	21.91		
Cu/Ce	1.67	1.94		

In the next phase of the project, the catalyst having Cu/Ce mass ratio of 4(Cu4Ce1) was chosen to represent the copper oxide catalyst modified by ceria, and the catalysts with Cu/Ce mass ratio of 1/3 (Cu1Ce3) was selected to represent the ceria-based catalysts to be tested with other reductants. Figure 7 shows that in the presence of water, while both catalysts can achieve almost total reduction of NO with propylene at high temperatures, the temperature for total conversion was significantly lower for Cu4Ce1 (673 K) compared to that for Cu1Ce3 (about 773 K).

Figure 8 demonstrates the effect of propylene to NO molar ratio on the NO conversion. It is seen that the reductant composition has a very pronounced effect on the temperature at which total conversion of NO was achieved in the concentration range studied in this research.

According to Figure 9, presence of water vapor has a slight adverse effect on the performance of the catalyst. The temperature for complete conversion of NO increased by about 25 K compared to that obtained with the dry gas.

Both catalysts were very effective in completely reducing the NO in the simulated Briggs and Stratton exhaust gas. In the temperature range employed, 473 K – 673 K, no NO or NO<sub>2</sub> were detected in the gas passed over the catalyst bed. Addition of 90 ppm SO<sub>2</sub> to the gas mixture poisoned the Cu4Ce1 catalyst irreversibly at 713 K. On the other hand, as seen in Figure 10, the poisoning effect of SO<sub>2</sub> on Cu1Ce3 could be partially reversed at the same temperature and almost completely reversed at higher temperatures by the addition of stoichiometric amount of oxygen. The 90 ppm SO<sub>2</sub> introduced is

significantly higher than the  $\text{SO}_2$  concentrations expected in a small engine exhaust (about 20 ppm), but due to the limitations of our experimental setup, 90 ppm was the lowest  $\text{SO}_2$  concentration that could be fed.

A set of catalysts were also prepared using the inexpensive, highly porous and light weight substrates supplied by Briggs and Stratton as catalyst support. These substrates were first coated by  $\gamma$ -alumina to impart microporosity, subsequently impregnated with the desired catalyst precursor solution, dried, and calcined. When these catalysts were used at 573 K with about the same space velocity (72,000/hr), complete conversion of NO to  $\text{N}_2$  were obtained.

## CONCLUSIONS

**With methane as the reductant:** As the copper to cerium ratio in the catalysts increases, conversion of NO is enhanced and complete conversion is approached. As expected, conversion increases with a reduction in space velocity. Ceria by itself is not a good catalyst for the reduction of NO in the absence of oxygen both in dry and wet gases. Addition of cerium oxide to copper oxide catalysts exhibits enhanced catalytic activity with wet gases. Used catalysts have about the same color as the fresh catalysts. Catalysts with copper to cerium ratio of less than 3 are inferior to copper. Catalysts with copper to cerium ratio higher than 3 have higher activities than copper oxide especially at lower temperatures. Catalyst with a copper to cerium ratio of 4 exhibits the best wet performance, corresponding to 95% NO conversion at 873 K.

**With propylene as the reductant:** With both high Cu and high Ce catalysts, high NO conversions were achieved at lower temperatures than those required for reduction with methane. When there was no  $\text{SO}_2$  in the gas, catalyst  $\text{Cu}_4\text{Ce}_1$  showed better performance than catalyst  $\text{Cu}_1\text{Ce}_3$ , but it was completely and irreversibly deactivated at 713 K by the addition of  $\text{SO}_2$ . Higher propylene to NO mole ratios reduced the temperature needed for complete NO conversion to  $\text{N}_2$ . In the absence of  $\text{SO}_2$ , the catalysts did not exhibit any deactivation over 15 cycles of 2-hour runs interspaced with 30 minutes storage under helium.

**With simulated Briggs and Stratton exhaust gas:** Both high Cu and high Ce catalysts reduced NO in the simulated exhaust gas completely to N<sub>2</sub> in the absence of SO<sub>2</sub>. The poisoning effect of SO<sub>2</sub> on the Cu<sub>1</sub>Ce<sub>3</sub> catalyst could be partially reversed by the addition of stoichiometric amount of oxygen and increasing the temperature of the catalyst bed. At 723 K, over 90 % conversion of NO to N<sub>2</sub> could be achieved after 18 operation cycles (2-hour runs with 30 min idle time under helium). It can be concluded that over 90 % reduction of NO could be achieved using the catalysts that were developed, even in the presence of 90 ppm SO<sub>2</sub>. As indicated above, 90 ppm SO<sub>2</sub> is more than the amount of SO<sub>2</sub> expected to be present in the small engine exhaust and the actual catalyst deactivation will probably be less than that experienced in our runs. Therefore, it is believed that the Cu<sub>1</sub>Ce<sub>3</sub> catalyst developed and tested in this research can be successfully used in a commercial catalytic muffler for small engines.

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Figure 1. Conversion as a function of reactor temperature for various catalyst samples. Space velocity = 93,000/h

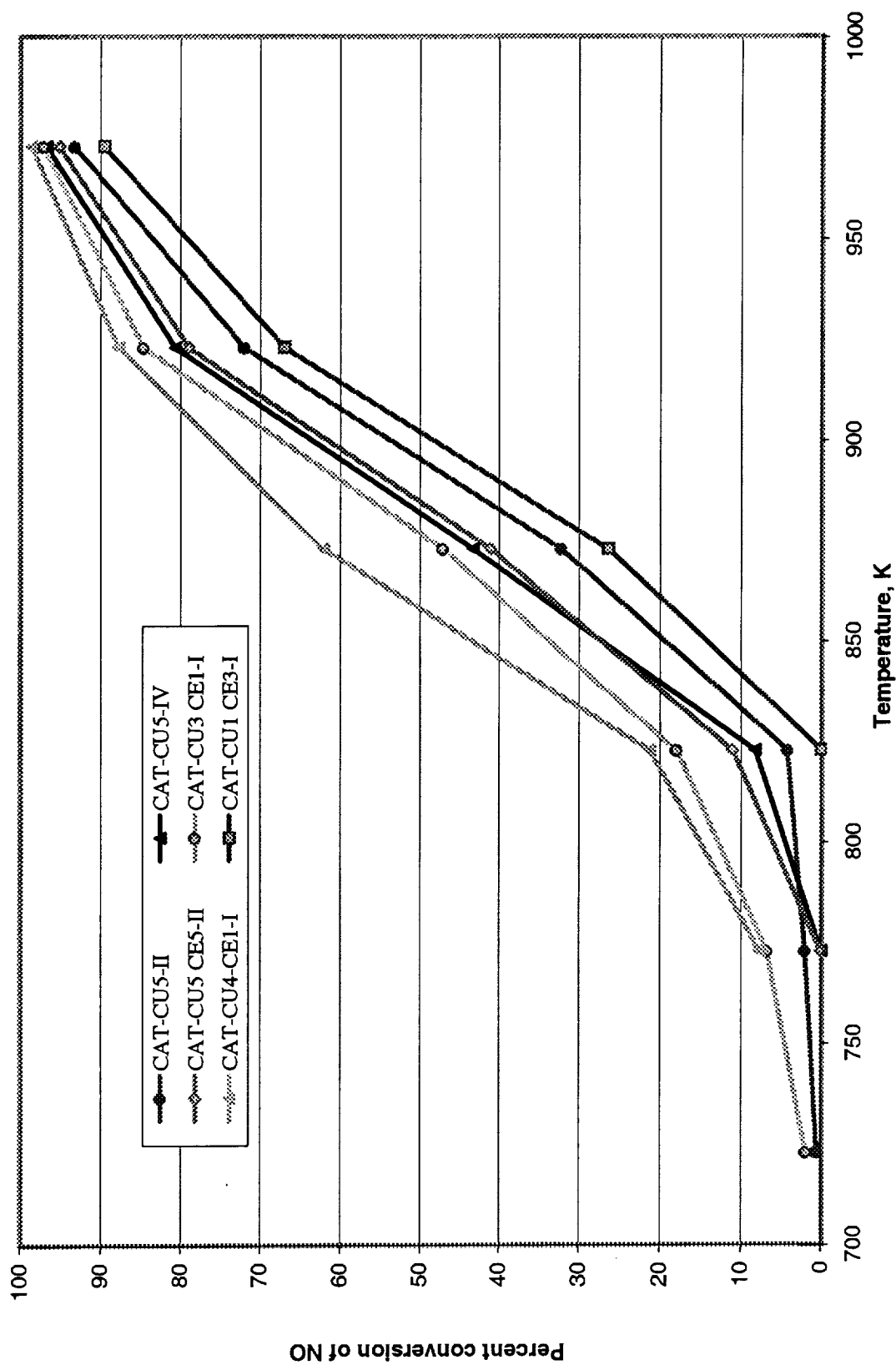


Figure 2. Conversion as a function of reactor temperature for various catalyst samples. Space velocity = 46500/h

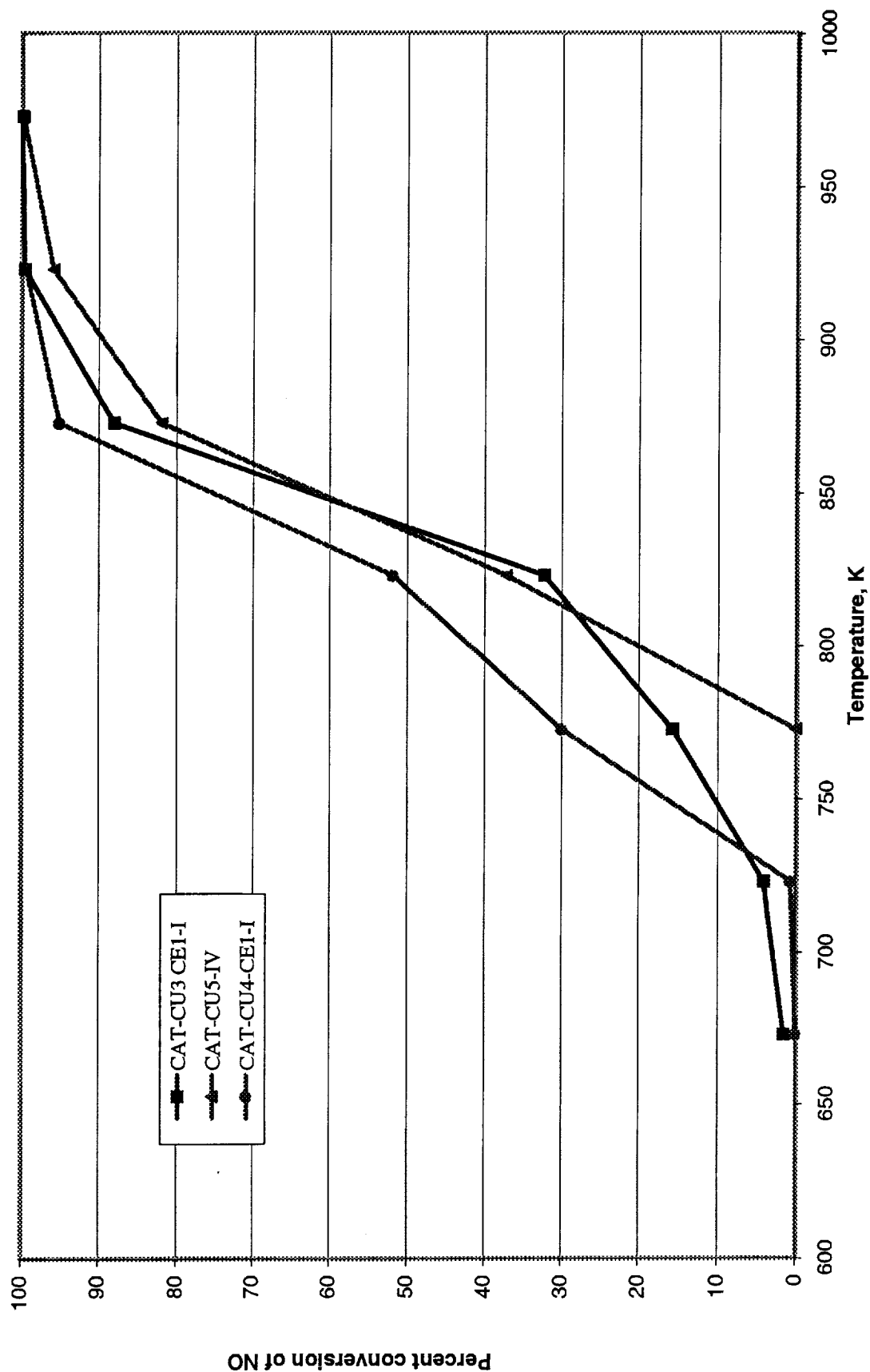


Figure 3. Effect of Space Velocity on Conversion for Various Catalyst Samples

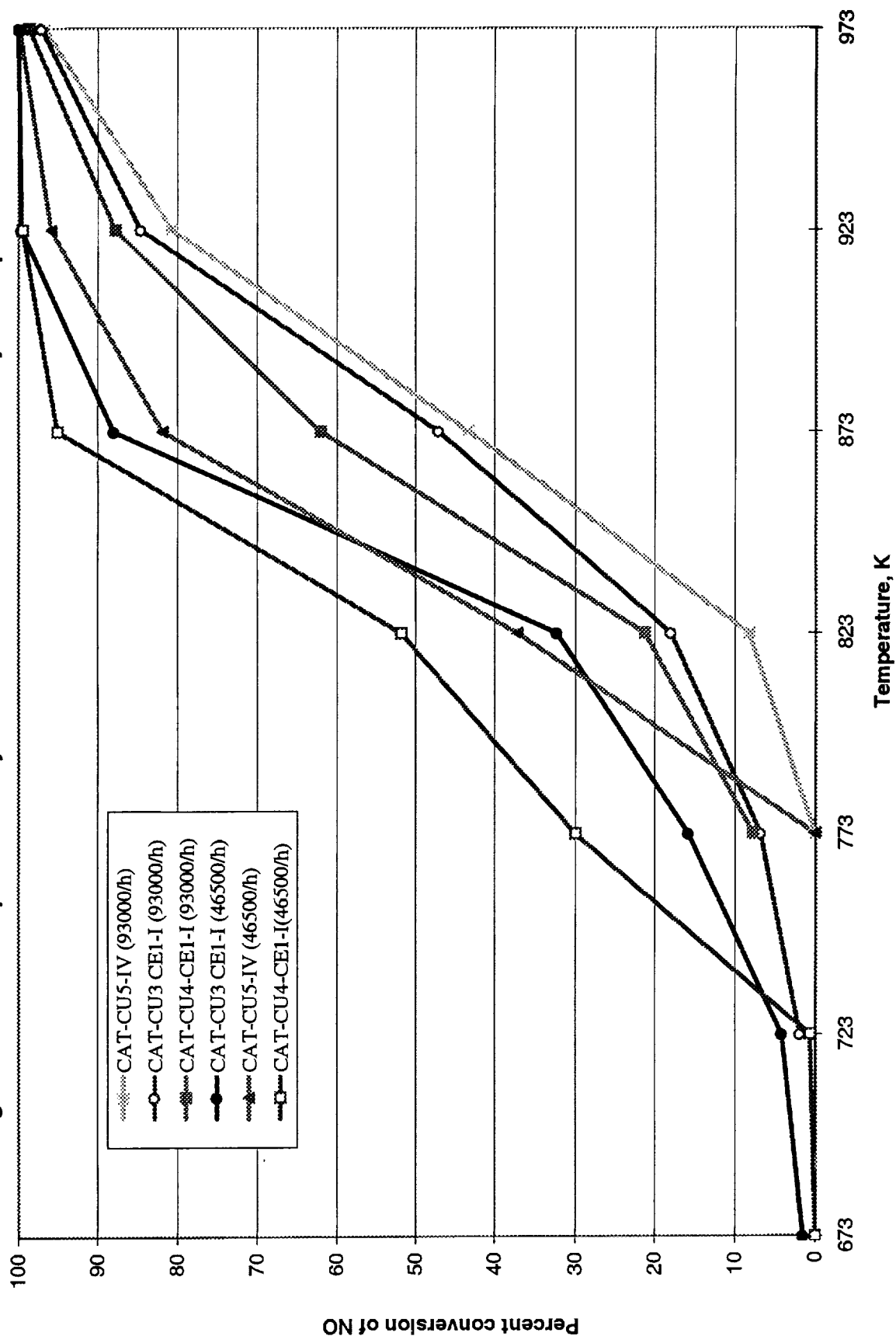
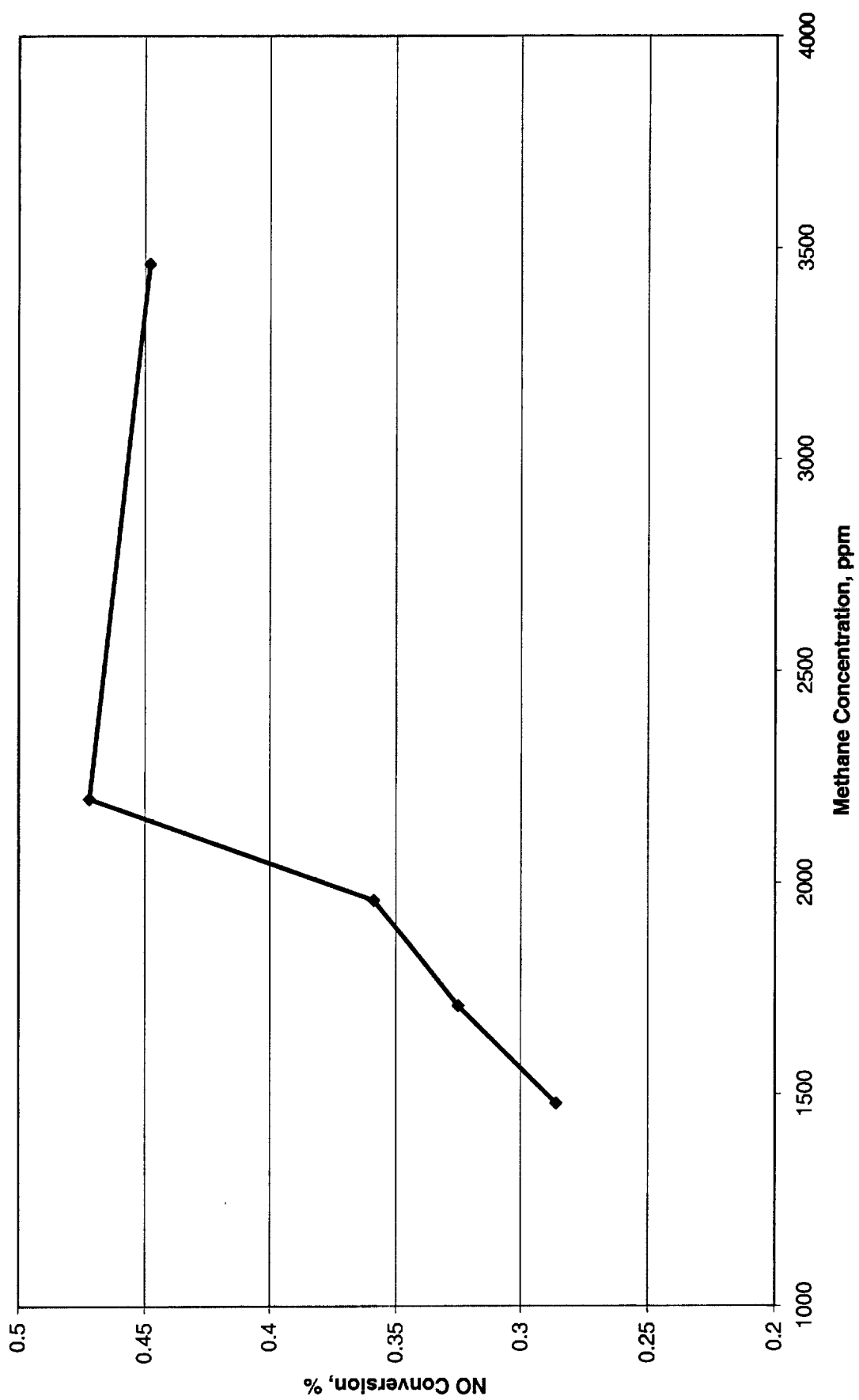
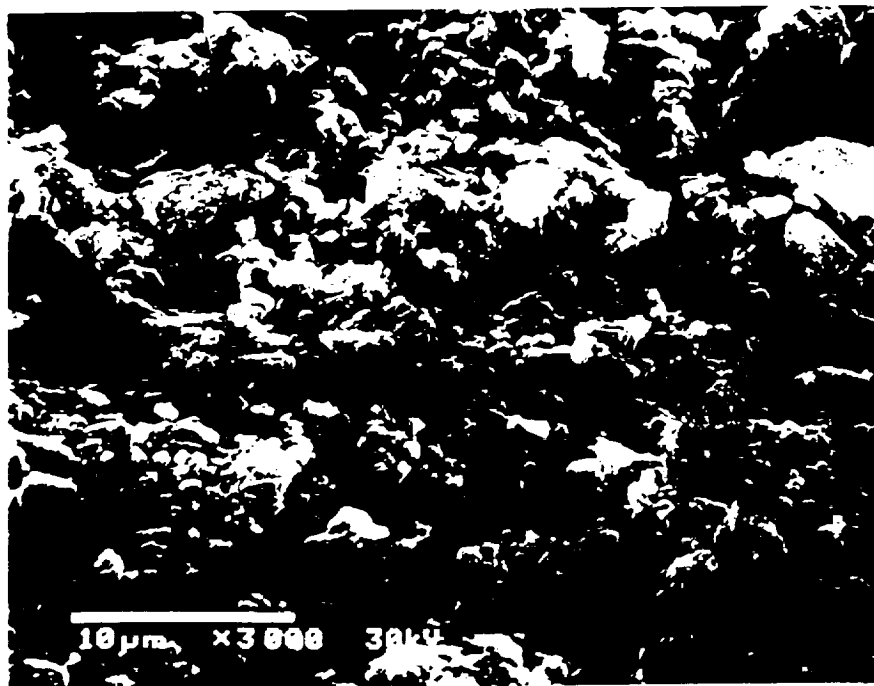


Figure 4. Effect of Methane concentration on NO Conversion. Cu5Ce5 Catalyst





(a)  $\text{Cu}_3\text{Ce}_1$

Figure 5. Scanning Electron Microscope Micrographs



(b)  $\text{Cu}_6\text{Ce}_1$

Figure 6. EDAX Measurements Mass percent of components at different locations in Cu6Ce1 pellet



	Wt% at 0 (Avg)	Wt% at 1	Wt% at 2	Wt % at 3
O	20.44	7.76	14.78	15.10
Al	54.44	54.23	54.90	56.16
Ce	6.56	9.66	6.57	0.46
Cu	18.56	28.35	23.75	28.29
Cu/Ce	2.83	2.93	6.57	61.50

Figure 7. Effect of Catalyst Composition on NO Conversion. Reductant: Propylene  
(Propylene:NO=2:1)

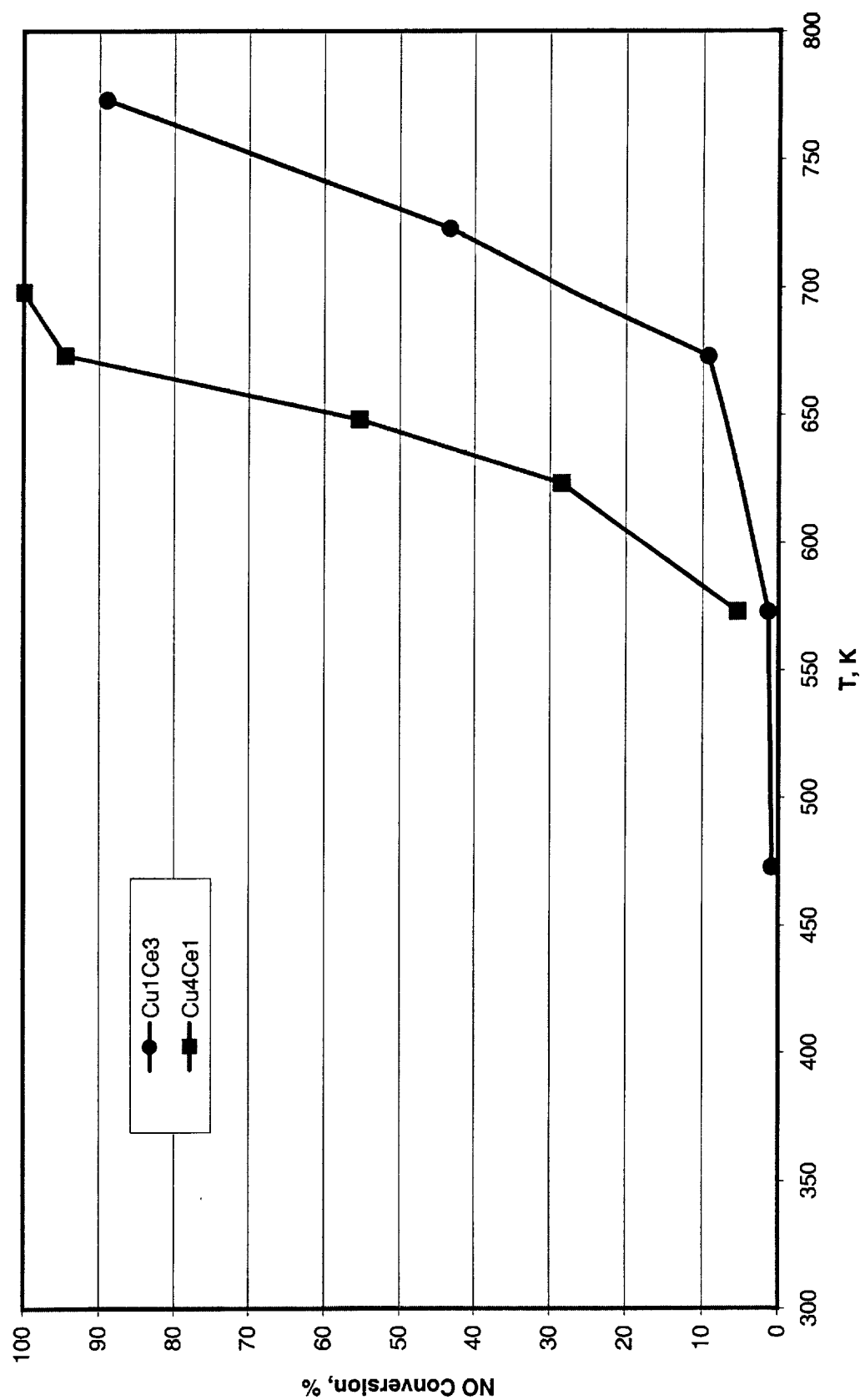


Figure 8. Effect of Reductant Concentration on NO Conversion. Catalyst: 4% Cu, 1% Ce  
Reductant: Propylene

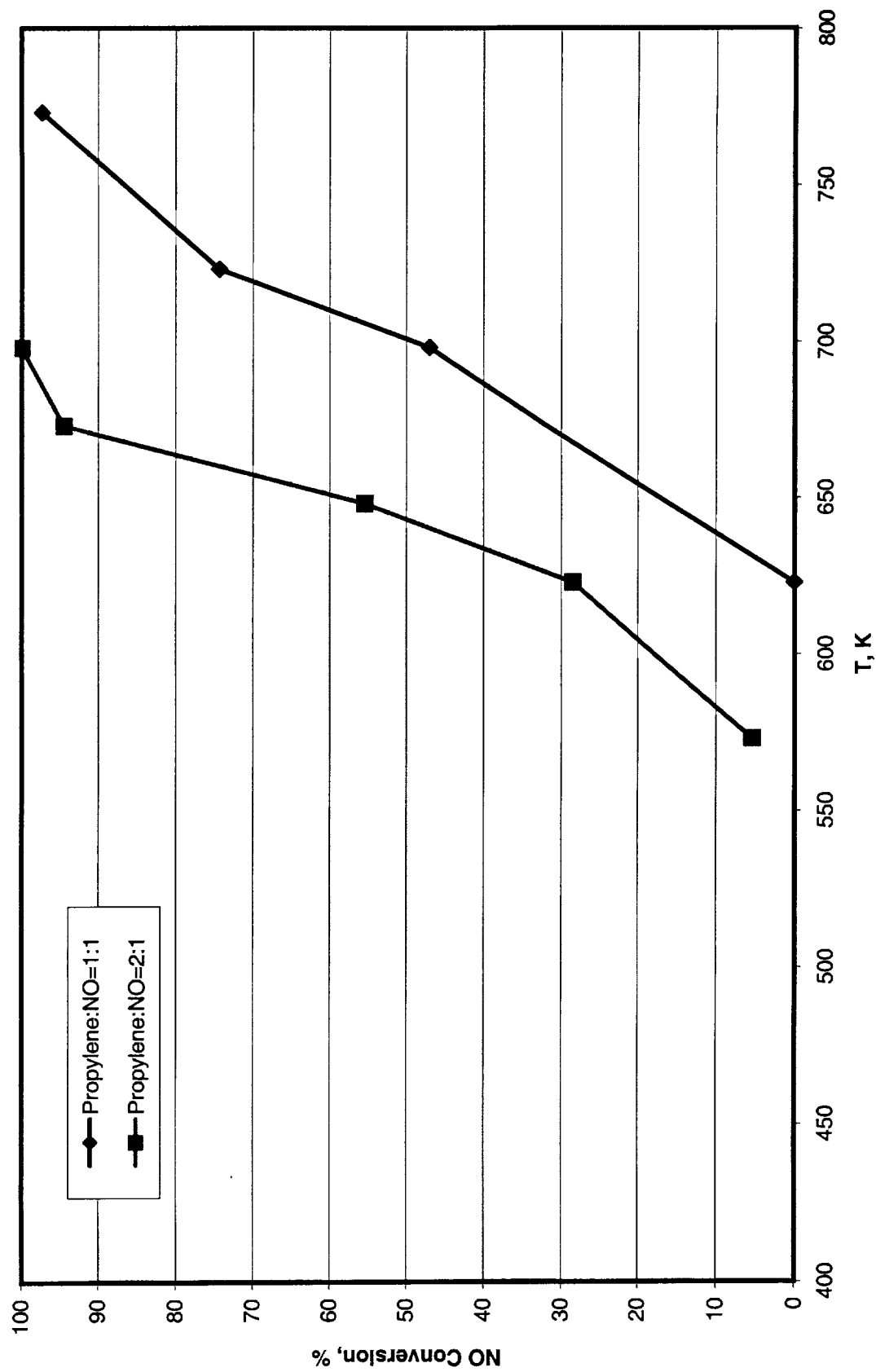




Figure 9. Effect of Water on NO Conversion. Catalyst 4% Cu 1% Ce. Reductant: Propylene  
(Propylene:NO ratio=2)

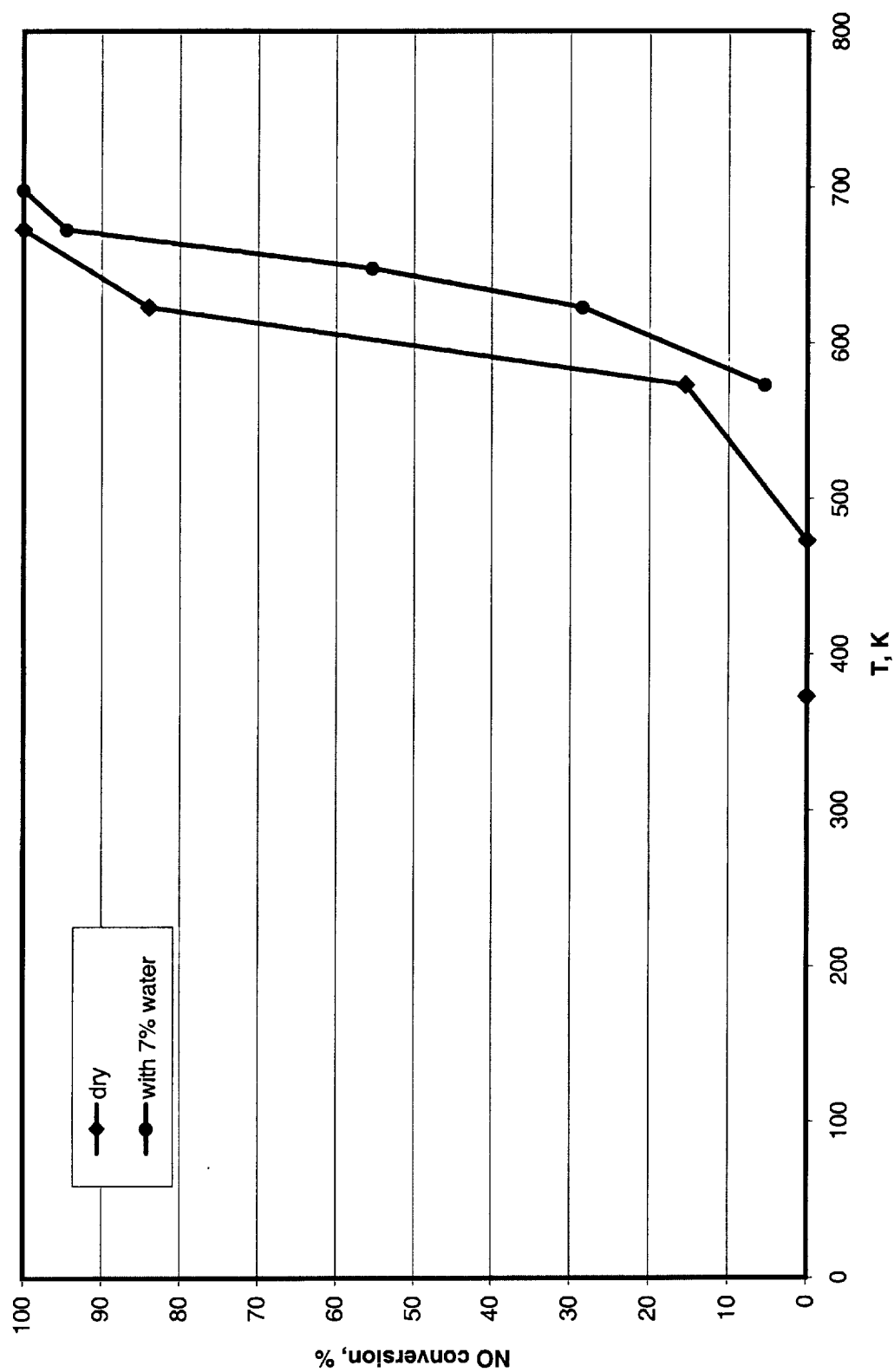


Figure 10. Effect of  $\text{SO}_2$  on NO Conversion

